

SPECIFICATION

GLASS ARTICLES WITH CONDUCTIVE ANTIREFLECTION COATING AND CATHODE-RAY TUBE USING THE SAME

TECHNICAL FIELD

The present invention relates to glass articles coated with an antireflection film combining electrical conductivity and light absorbing properties. More particularly, the present invention relates to glass articles such as a face plate for use in displays in which a fluorescent substance is excited by accelerated electron rays to display an image, e.g., cathode-ray tubes, and as a glass plate to be bonded to the front side of the display area of such a face plate with an adhesive, e.g., a resin or glass frit. The present invention further relates to a cathode-ray tube using the same.

BACKGROUND ART

In displays using a cathode-ray tube, such as television receivers, measures are being taken to diminish the reflection of external light from the display surface to improve display quality. Since a high voltage is used in these displays using a cathode-ray tube because of the use of an electron gun therein, the image display surface is electrostatically charged and thus attracts dust particles floating in the air. Measures are hence being taken to impart electrical conductivity to the front side of a display in order to prevent or inhibit the phenomenon

attributable to electrostatic charging.

Furthermore, it has been pointed out that electron rays accelerated by a high voltage generate electromagnetic wave and this electromagnetic wave may exert an adverse influence on the human body. Displays are hence being produced in which the front side of the display area is coated with a conductive coating film for electromagnetic wave shielding.

For the above-described purposes, a technique is being employed in which a glass plate coated with a conductive antireflection film is bonded to the face plate of a cathode-ray tube or the outer surface of a face plate is directly coated with a conductive antireflection film.

Examples of such conductive antireflection films for use as coating films on glass articles for the purpose of improving the display quality of cathode-ray tubes include the multilayer structure represented by glass plate/metal/titanium oxide/silicon oxide as disclosed in JP-A-64-70701 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), the multilayer structure represented by glass plate/magnesium fluoride/metal/titanium oxide/magnesium fluoride as disclosed in JP-A-1-180333, and the multilayer structure represented by glass/praseodymium titanate/metal/praseodymium titanate/magnesium fluoride as disclosed in Japanese Patent No. 2,565,538.

The metal films disclosed in the above references for use in those prior art techniques are thin films of stainless steel, titanium, chromium, zirconium, molybdenum and nickel.

However, conductive antireflection films having a multilayer structure comprising at least one metal film made of any of the metals and alloy shown in the above references and one or more transparent dielectric films have a problem that when the metal film has a thickness reduced to 5 nm or smaller so as to attain a high visible ray transmittance, the antireflection film has markedly increased electrical resistance, resulting in considerably impaired antistatic properties and electromagnetic wave shielding properties.

Furthermore, an antireflection film containing a metal film made of any of the metals and alloy shown in the references cited above has drawbacks when applied to a cathode-ray tube production process in which the antireflection film is formed on the front side of a face plate made of glass and this coated face plate is bonded to a funnel with a glass frit with heating. Specifically, in the step of bonding with heating, the electrical resistance of the conductive antireflection film increases considerably and the transmittance also increases. It has hence been difficult to produce a cathode-ray tube having both light-absorbing properties and excellent antistatic properties. In other words, any prior art technique has not succeeded in accomplishing the subject of forming a conductive antireflection film which changes little in electrical resistance or visible ray transmittance even when heated in cathode-ray tube assembling.

DISCLOSURE OF THE INVENTION

A first object of the present invention is to provide a

glass article having conductive antireflection coating, as a first glass article, which comprises a glass substrate having a refractive index of from 1.4 to 1.7 as measured at a wavelength of 550 nm and a conductive antireflection film comprising superposed layers comprising, formed on the glass substrate in this order, a first layer which is a metal film, a second layer which is a high-refractive-index transparent dielectric film having a refractive index of from 2.0 to 2.4 as measured at a wavelength of 550 nm, and a third layer which is a low-refractive-index transparent dielectric film having a refractive index of from 1.35 to 1.46 as measured at a wavelength of 550 nm, said metal film being a film of a nickel-iron alloy, and said glass article having a visible ray reflectance of 1% or lower. (hereinafter referred to as a "first embodiment").

A second object of the present invention is to provide a glass article having conductive antireflection coating, as a second glass article, which comprises a glass substrate having a refractive index of from 1.4 to 1.7 as measured at a wavelength of 550 nm and a conductive antireflection film comprising superposed layers comprising, formed on the glass substrate in this order, a first layer which is a metal film, a second layer which is a high-refractive-index transparent dielectric film having a refractive index of from 2.0 to 2.4 as measured at a wavelength of 550 nm, a third layer which is a medium-refractive-index transparent dielectric film having a refractive index of from 1.7 to 1.9 as measured at a wavelength of 550 nm, and a fourth layer which is a low-refractive-index transparent

dielectric film having a refractive index of from 1.35 to 1.46 as measured at a wavelength of 550 nm, said metal film being a film of a nickel-iron alloy, and said glass article having a visible ray reflectance of 1% or lower. (hereinafter referred to as a "second embodiment").

A third object of the present invention is to provide a glass article having conductive antireflection coating, as a third glass article, which comprises a glass substrate having a refractive index of from 1.4 to 1.7 as measured at a wavelength of 550 nm and a conductive antireflection film comprising superposed layers comprising, formed on the glass substrate in this order, a first layer which is a metal film, a second layer which is a high-refractive-index transparent dielectric film having a refractive index of from 2.0 to 2.4 as measured at a wavelength of 550 nm, a third layer which is a metal film, a fourth layer which is a high-refractive-index transparent dielectric film having a refractive index of from 2.0 to 2.4 as measured at a wavelength of 550 nm, and a fifth layer which is a low-refractive-index transparent dielectric film having a refractive index of from 1.35 to 1.46 as measured at a wavelength of 550 nm, at least one of the metal films respectively as the first and third layers being a film of a nickel-iron alloy, and said glass article having a visible ray reflectance of 1% or lower. (hereinafter referred as to a "third embodiment").

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view of one embodiment of the glass

articles having conductive antireflection coating of the present invention. Fig. 2 is partial sectional views for explaining the multilayer structures of conductive antireflection films according to the present invention. Fig. 3 is a graph showing the visible-region transmission/reflection characteristics of the Example according to the present invention.

The numerals in the drawings show as follows. 1: Glass article having conductive antireflection coating, 2: Conductive antireflection film, 3: Glass substrate, 4: Metal film, 5: High-refractive-index transparent dielectric film, 6: Low-refractive-index transparent dielectric film, 7: Medium-refractive-index transparent dielectric film, 8: Undercoat film

BEST MODE FOR PRACTICING THE INVENTION

The metal film in the first embodiment of the present invention should be a film of an alloy of nickel and iron. The nickel content of the metal film is preferably 5% by weight or higher, more preferably 10% by weight or higher. The most preferred nickel content thereof is 70% by weight or higher. Nickel contents thereof lower than 5% by weight are undesirable in that the metal film has thermal properties similar to those of metal films made of iron alone and undergoes a considerable increase in electrical resistivity and a considerable change in transmittance upon heating.

The nickel content of the metal film is preferably 95% by weight or lower. Nickel contents thereof exceeding 95% by weight are undesirable in that the metal film has thermal

properties similar to those of metal films made of nickel alone and has an exceedingly high electrical resistivity especially when the thickness thereof is smaller than 4 nm.

In the first embodiment of the present invention, the thickness of the metal film is preferably from 1.5 to 8 nm. Thicknesses thereof smaller than 1.5 nm are undesirable in that the metal film has an exceedingly high electrical resistivity. On the other hand, thicknesses thereof exceeding 8 nm are undesirable in that the metal film has a reduced transmittance, resulting in darkened displayed images.

In the first embodiment of the present invention, a visible ray reflectance is regulated so as to be 1% or lower. Furthermore, from the standpoint of preventing the glass article from producing a reflection of a conspicuous color tone when it is used in a cathode-ray tube, the thickness of the high-refractive-index transparent dielectric film as the second layer is preferably from 5 to 140 nm and that of the low-refractive-index transparent dielectric film as the third layer is preferably from 50 to 120 nm.

The metal film in the second embodiment of the present invention should be a film of an alloy of nickel and iron. The nickel content of the metal film is preferably 5% by weight or higher, more preferably 10% by weight or higher, most preferably 70% by weight or higher. Nickel contents thereof lower than 5% by weight are undesirable in that the metal film has thermal properties similar to those of metal films made of iron alone and undergoes a considerable increase in electrical resistivity and

a considerable change in transmittance upon heating.

The nickel content of the metal film is preferably 95% by weight or lower. Nickel contents thereof exceeding 95% by weight are undesirable in that the metal film has thermal properties similar to those of metal films made of nickel alone and has an exceedingly high electrical resistivity especially when the thickness thereof is smaller than 4 nm.

In the second embodiment of the present invention, the thickness of the metal film is preferably from 1.5 to 8 nm. Thicknesses thereof smaller than 1.5 nm are undesirable in that the metal film has an exceedingly high electrical resistivity. On the other hand, thicknesses thereof exceeding 8 nm are undesirable in that the metal film has a reduced transmittance, resulting in darkened displayed images.

In the second embodiment of the present invention, a visible ray reflectance is regulated so as to be 1% or lower. Furthermore, from the standpoint of preventing the glass article from producing a reflection of a conspicuous color tone when it is used in a cathode-ray tube, the thickness of the high-refractive-index transparent dielectric film as the second layer is preferably from 5 to 70 nm, that of the medium-refractive-index transparent dielectric film as the third layer is preferably from 10 to 100 nm, and that of the low-refractive-index transparent dielectric film as the fourth layer is preferably from 50 to 120 nm.

In the third embodiment of the present invention also, the metal film should be a film of an alloy of nickel and iron.

The nickel content of the metal film is preferably 5% by weight or higher, more preferably 10% by weight or higher, most preferably 70% by weight or higher. Nickel contents thereof lower than 5% by weight are undesirable in that the metal film has thermal properties similar to those of metal films made of iron alone and undergoes a considerable increase in electrical resistivity and a considerable change in transmittance upon heating.

The nickel content of the metal film is preferably 95% by weight or lower. Nickel contents thereof exceeding 95% by weight are undesirable in that the metal film has thermal properties similar to those of metal films made of nickel alone and has an exceedingly high electrical resistivity especially when the thickness thereof is smaller than 4 nm.

In the third embodiment of the present invention, the metal films respectively as the first and third layers each preferably has a thickness of from 1.5 to 7.5 nm and the total thickness thereof is preferably 9 nm or smaller. The reasons for the limitation of the thickness of each metal layer are the same as in the first and second embodiments described above. Total thicknesses thereof exceeding 9 nm are undesirable when the antireflection film is used on the front side of a display, because the film has reduced transparency, resulting in darkened displayed images.

In the third embodiment of the present invention, a visible ray reflectance is regulated so as to be 1% or lower. Furthermore, from the standpoint of preventing the glass article from producing a reflection of a conspicuous color tone when it

is used in a cathode-ray tube, the thickness of the high-refractive-index transparent dielectric film as the second layer is preferably from 10 to 70 nm, that of the high-refractive-index transparent dielectric film as the fourth layer is preferably from 10 to 70 nm, and that of the low-refractive-index transparent dielectric film as the fifth layer is preferably from 70 to 120 nm.

In each of the first, second and third embodiments of the present invention, the glass substrate can be a face plate made of a glass or a transparent or colorless glass plate. These glass substrates are not particularly limited in glass composition. For example, a glass substrate which has a soda-lime silicate composition, borosilicate composition, aluminosilicate composition, or aluminoborosilicate composition can be used, if desired, after having undergone a processing such as bending or tempering.

Examples of the high-refractive-index transparent dielectric film(s) in each of the first, second and third embodiments of the present invention include films of praseodymium titanate (PrTiO_3), titanium oxide (TiO_2), tantalum oxide (Ta_2O_5), and zirconium oxide (ZrO_2). Preferred of these is praseodymium titanate. This is because a transparent and dense film of praseodymium titanate can be formed by vapor deposition without the necessity of introducing oxygen gas for the deposition and, hence, the metal film being formed can be prevented from suffering oxidative deterioration.

Examples of the material of the low-refractive-index

transparent dielectric film in each of the first, second and third embodiments of the present invention include magnesium fluoride and silicon dioxide. Preferred of these is magnesium fluoride because the refractive index of magnesium fluoride is as low as 1.35. Namely, a large difference in refractive index is obtained between a film of magnesium fluoride and a high-refractive-index transparent dielectric film, whereby a reduction in reflectance is easy.

Examples of the material of the medium-refractive-index transparent dielectric film in the second embodiment of the present invention include magnesium oxide (MgO), niobium oxide (Nb_2O_5), and silicon monoxide (SiO). Preferred of these is magnesium oxide. This is because a transparent and dense film of magnesium oxide can be formed by vapor deposition without the necessity of introducing oxygen gas for the deposition and, hence, the metal film being formed can be prevented from suffering oxidative deterioration.

In each of the first, second and third embodiments of the present invention, a transparent dielectric layer (hereinafter referred to as "undercoat film") can be formed between the glass substrate and the metal film as the first layer. This undercoat film is formed for the purpose of preventing the glass surface from being in contact with the metal film as the first layer, i.e., preventing impurities such as water present on the glass surface from coming into the metal film, to increase the electrical resistance of the metal film.

The material constituting the undercoat film is not

particularly limited. However, preferred examples thereof include praseodymium titanate, magnesium oxide, and magnesium fluoride (MgF_2).

The thickness of the undercoat film is preferably 3 nm or larger from the standpoint of enabling a smooth metal film to be formed as the first layer to thereby make the metal film have reduced electrical resistance. From the standpoint of diminishing the surface roughness of the undercoat film itself, the thickness thereof is preferably 7 nm or smaller, more preferably 5 nm or smaller.

A third metal may be incorporated into the metal layer comprising nickel and iron in each of the first, second and third embodiments of the present invention for the purpose of, e.g., subtly regulating the degree of light absorption or the color tone of a reflection, as long as the incorporation of the third metal does not considerably impair the heat resistance of the metal layer.

Each constituent layer of the conductive antireflection film in each of the first, second and third embodiments of the present invention can be formed by a conventional technique such as vapor deposition or ion plating.

The cathode-ray tube according to the present invention can be produced by a method comprising bonding a face plate coated with a conductive antireflection film according to the present invention to a funnel with heating, or by a method comprising bonding a face plate to a funnel and then coating the face plate with a conductive antireflection film according to the present

invention.

The present invention will be explained below by reference to the drawings and Examples.

Fig. 1 is a sectional view of one embodiment of an article having conductive antireflection coating 1 of the present invention. This article 1 comprises a face plate 3 made of glass and a conductive antireflection film 2 with which an image display area of the face plate 3 is coated.

Fig. 2 are partial sectional views for explaining the multilayer structures of conductive antireflection films 2 according to the present invention. The conductive antireflection film 2 shown in Fig. 2 (a) is comprised of, formed on a face plate 3 in this order, a metal film 4, a high-refractive-index transparent dielectric film 5, and a low-refractive-index transparent dielectric film 6. The conductive antireflection film 2 shown in Fig. 2 (b) is comprised of, formed on a face plate 3 in this order, a metal film 4, a high-refractive-index transparent dielectric film 5, a medium-refractive-index transparent dielectric film 7, and a low-refractive-index transparent dielectric film 6. The conductive antireflection film 2 shown in Fig. 2 (c) is comprised of, formed on a face plate 3 in this order, an undercoat film 8, a metal film 4, a high-refractive-index transparent dielectric film 5, a metal film 4, a high-refractive-index transparent dielectric film 5, and a low-refractive-index transparent dielectric film 6.

Fig. 3 shows a graphic presentation illustrating the visible-region reflection/transmission spectral

characteristics of the sample obtained in Example 6 according to the present invention.

In the Examples and Comparative Examples given below, the following materials were used for forming the respective films by vapor deposition.

- Nickel-iron films in the Examples: nickel-iron alloy wires having given compositions.
- Nickel films in Comparative Examples 1 and 3: nickel wire.
- Iron film in Comparative Example 2: iron wire.
- Nickel-iron-chromium films in Comparative Examples 4 and 5: nickel-iron-chromium alloy wires having given compositions.
- Nickel-chromium film in Comparative Example 6: nickel-chromium alloy wire having a given composition.
- Praseodymium titanate film: pellet of SUBSTANCE H2 (trade name), manufactured by Merck & Co., Inc.
- Magnesium oxide films: granular magnesium oxide.
- Magnesium fluoride films: granular magnesium fluoride.

EXAMPLE 1

A sufficiently cleaned soda-lime silicate glass plate having dimensions of 100 mm by 100 mm by 3 mm (thickness) was placed in a vacuum deposition vessel and heated to 300°C with a substrate heater disposed in the vapor deposition apparatus. While the glass plate was kept being thus heated, a conductive antireflection film having the multilayer structure shown in the column of Example 1 in Table 1 was deposited on the glass plate. For vaporizing the vapor deposition materials, the electron beam

deposition method was used. The distance between the crucible containing each deposition material and the glass plate was adjusted to 100 cm, and the deposition was conducted while rotating the glass plate. Prior to the deposition of each constituent film, the vessel was evacuated with an oil diffusion pump to a vacuum of 0.003 Pa. In depositing the nickel-iron alloy, praseodymium titanate, magnesium fluoride and magnesium oxide films, oxygen gas was not introduced.

The sample obtained was taken out of the vapor deposition apparatus and examined for transmittance (wavelength: 550 nm), reflectance on the coating side (wavelength: 550 nm), and sheet resistivity as a measure of antistatic properties. The composition of the metal film was determined by chemical analysis. The results of the above examinations and determination are shown in Table 2. Furthermore, the sample was heat-treated in the air at 450°C for 1 hour and then examined for transmittance, reflectance on the coating side, and sheet resistivity. The results obtained are shown in the column of Example 1 in Table 2.

The sample had a reflectance of 1% or lower, which is necessary for practical use. The reflectance thereof changed little through the heat treatment and remained 1% or lower. The sheet resistivity of the sample was $282 \Omega/\square$, which is sufficiently low for antistatic properties. Through the heat treatment, the resistivity of the sample decreased rather than deteriorated (increased). The transmittance of the sample changed from 66.5% to 67.2%, and the change thereof was as small as 0.7%. The value

of transmittance after the heat treatment was within the range of from 40 to 80%, which is desired for the face plates of cathode-ray tubes or for front glass panels to be bonded to transparent face plates.

EXAMPLES 2 TO 10

In the same manner as in Example 1, conductive antireflection films respectively having the layer constitutions shown in Table 1 were deposited on glass plates. The samples thus obtained were subjected to the same tests as in Example 1, and the results obtained are shown in Table 2. The reflectances of the samples of Examples 2 to 10 were 1% or lower both in the initial stage and after the heat treatment. The sheet resistivities of the samples were as low as below 500 $\Omega/\square$ in the initial stage and were found to decrease through the heat treatment rather than increase considerably. The change in transmittance through the heat treatment was as small as 2.2% or below in each sample.

The sample of Example 4 had the same film constitution as that of Example 2, except that the former additionally had an undercoat film of praseodymium titanate. The sample of Example 7 had the same film constitution as that of Example 6, except that the former additionally had an undercoat film of praseodymium titanate. Comparisons between Examples 2 and 4 and between Examples 6 and 7 show that the additional formation of the undercoat film was effective in reducing the sheet resistivity.

Table 1

Example	Film 1	Film 2	Film 3	Film 4	Film 5	Film 6	Composition of metal film
1	NiFe (3.2)	PrTiO ₃ (127.4)	MgO (45.4)	MgF ₂ (71.7)			Fe/Ni 20/80
2	NiFe (3.2)	PrTiO ₃ (127.4)	MgO (45.4)	MgF ₂ (71.7)			Fe/Ni 10/90
3	NiFe (3.2)	PrTiO ₃ (127.4)	MgO (45.4)	MgF ₂ (71.7)			Fe/Ni 30/70
4	PrTiO ₃ (5.0)	NiFe (2.0)	PrTiO ₃ (101.4)	MgO (36.3)	MgF ₂ (80.8)		Fe/Ni 20/80
5	PrTiO ₃ (5.0)	NiFe (3.2)	PrTiO ₃ (134.5)	MgF ₂ (96.8)			Fe/Ni 50/50
6	NiFe (4.6)	PrTiO ₃ (26.0)	NiFe (2.4)	PrTiO ₃ (35.0)	MgF ₂ (79.0)		Fe/Ni 20/80
7	MgO (5.0)	NiFe (4.6)	PrTiO ₃ (26.0)	NiFe (2.4)	PrTiO ₃ (35.0)	MgF ₂ (79.0)	Fe/Ni 40/60
8	PrTiO ₃ (5.0)	NiFe (2.2)	PrTiO ₃ (34.8)	MgF ₂ (93.6)			Fe/Ni 95/5
9	PrTiO ₃ (5.0)	NiFe (2.4)	PrTiO ₃ (34.8)	MgF ₂ (93.6)			Fe/Ni 5/95
10	NiFe (3.2)	PrTiO ₃ (34.8)	MgF ₂ (93.6)				Fe/Ni 5/95

Upper expression is a material of a film, lower expression is a thickness of a film (unit: nm), and compositions of a metal film are by wt%.

Table 2

Example	Transmittance (%)			Reflectance (%)			Sheet resistivity ($\Omega/\square$)		
	Before	After	Difference	Before	After	Difference	Before	After	Difference
Example 1	66.5	67.2	0.7	0.22	0.25	0.03	282	258	-24
Example 2	65.2	66.3	1.1	0.26	0.28	0.02	305	245	-60
Example 3	66.0	67.8	1.8	0.23	0.29	0.06	295	226	-69
Example 4	75.2	76.2	1.0	0.25	0.26	0.01	207	174	-33
Example 5	67.0	67.7	0.7	0.19	0.30	0.11	198	184	-14
Example 6	47.0	49.2	2.2	0.11	0.28	0.17	98	96	-2
Example 7	46.6	47.5	0.9	0.17	0.20	0.03	87	85	-2
Example 8	61.2	61.8	0.6	0.81	0.85	0.04	341	330	-11
Example 9	70.2	70.2	0.0	0.70	0.50	0.20	279	247	-32
Example 10	67.2	67.6	0.4	0.34	0.41	0.07	486	484	-2

Before: before heat treatment

After: after heat treatment

Difference: (value after heat treatment)-(value before heat treatment)

COMPARATIVE EXAMPLE 1

A conductive antireflection film having the layer constitution shown in the column Comparative Example 1 in Table 3, in which the metal film was made of nickel alone, was deposited in the same manner as in Example 1 to obtain a comparative sample. This comparative sample was evaluated by the same methods as in Example 1, and the results obtained are shown in the column of Comparative Example 1 in Table 4. This comparative sample had reflectances of 1% or lower and showed satisfactory thermal stability of transmittance. However, the sheet resistivity thereof was higher than $2\text{ M}\Omega/\square$ both in the initial stage and after the heat treatment, showing that the comparative sample failed to have satisfactory antistatic properties.

COMPARATIVE EXAMPLE 2

A conductive antireflection film having the layer

constitution shown in the column Comparative Example 2 in Table 3, in which the metal film was made of iron alone, was deposited in the same manner as in Example 1 to obtain a comparative sample. This comparative sample was evaluated by the same methods as in Example 1, and the results obtained are shown in the column of Comparative Example 2 in Table 4. Although this comparative sample initially had a reflectance as low as 0.43%, the transmittance and reflectance thereof increased to 18.7% and 4.08%, respectively, through the heat treatment. Furthermore, the sheet resistivity thereof was higher than $2 \text{ M}\Omega/\square$ both in the initial stage and after the heat treatment, showing that the comparative sample failed to have satisfactory antistatic properties.

COMPARATIVE EXAMPLE 3

A conductive antireflection film having the layer constitution shown in the column of Comparative Example 3 in Table 3 was deposited to obtain a comparative sample. This layer constitution contained a metal film made of nickel alone and an undercoat film of praseodymium titanate interposed between the glass plate and the metal film as the first layer. This comparative sample was evaluated by the same methods as in Example 1, and the results obtained are shown in the column of Comparative Example 3 in Table 4. This comparative sample had reflectances of 1% or lower before and after the heat treatment and showed satisfactory thermal stability of transmittance. However, the sheet resistivity thereof was higher than $2 \text{ M}\Omega/\square$ both in the initial stage and after the heat treatment, showing that the

comparative sample failed to have satisfactory antistatic properties.

COMPARATIVE EXAMPLES 4 AND 5

Conductive antireflection films respectively having the layer constitutions shown in the columns of Comparative Example 4 and Comparative Example 5 in Table 3 were deposited to obtain comparative samples. In these layer constitutions, the metal films each was a ternary film of nickel, iron, and chromium. These comparative samples were evaluated by the same methods as in Example 1, and the results obtained are shown in the columns of Comparative Example 4 and Comparative Example 5 in Table 4. The transmittance of the comparative sample 4, in which the metal film had a chromium content of 28% by weight, increased by 9.8% through the heat treatment, while that of the comparative sample 5, in which each metal film had a chromium content of 16%, increased by 9.2% through the heat treatment. These comparative samples were thus found to have considerably poor thermal stability of transmittance. The sheet resistivities thereof were irregularly changed. That is, the sheet resistivity of the comparative sample 4 increased through the heat treatment, while that of the comparative sample 5 decreased.

COMPARATIVE EXAMPLE 6

A comparative sample was obtained in the same manner as in Comparative Example 1, except that in place of the metal film, a nickel-chromium binary film was formed. As shown in the column of Comparative Example 6 in Table 4, this comparative sample, through the heat treatment, underwent a change in transmittance

as large as 12.5%, and the sheet resistivity thereof increased by three orders of magnitude.

Table 3

Comparative Example	Film 1	Film 2	Film 3	Film 4	Film 5	Film 6	Composition of metal film
1	Ni (3.2)	PrTiO ₃ (127.4)	MgO (45.4)	MgF ₂ (71.7)			Ni 100
2	Fe (3.2)	PrTiO ₃ (127.4)	MgO (45.4)	MgF ₂ (71.7)			Fe 100
3	PrTiO ₃ (5.0)	Ni (3.2)	PrTiO ₃ (134.5)	MgF ₂ (96.8)			Ni 100
4	NiFeCr (3.2)	PrTiO ₃ (127.4)	MgO (45.4)	MgF ₂ (71.7)			Ni/Fe/Cr 60/12/28
5	NiFeCr (4.6)	PrTiO ₃ (26.0)	NiFeCr (2.4)	PrTiO ₃ (35.0)	MgF ₂ (79.0)		Ni/Fe/Cr 75/9/16
6	NiCr (3.2)	PrTiO ₃ (127.4)	MgO (45.4)	MgF ₂ (71.7)			Ni/Cr 80/20

Upper expression is a material of a film, lower expression is a thickness of a film (unit: nm), and compositions of a metal film is by wt%.

Table 4

Example	Transmittance (%)			Reflectance (%)			Sheet resistivity ($\Omega/\square$)		
	Before	After	Difference	Before	After	Difference	Before	After	Difference
Comparative Example 1	62.6	63.1	0.5	0.45	0.58	0.13	>2M	>2M	
Comparative Example 2	64.3	83.0	18.7	0.43	4.20	4.08	>2M	>2M	
Comparative Example 3	63.6	64.2	0.6	0.65	0.52	-0.13	>2M	>2M	
Comparative Example 4	66.7	76.5	9.8	0.37	1.54	1.17	1140	2950	1810
Comparative Example 5	47.3	56.5	9.2	0.25	0.34	0.09	1173	554	-619
Comparative Example 6	63.2	75.7	12.5	0.51	3.10	2.59	769	406K	

Before: before heat treatment

After: after heat treatment

Difference: (value after heat treatment)-(value before heat treatment)

As described above, none of the comparative samples were stable in both transmittance and sheet resistivity to the heat treatment. In contrast, in each of the samples of the Examples according to the present invention, the transmittance and reflectance thereof were stable to the heat treatment. The sheet resistivities thereof decreased through the heat treatment rather than increased. These results show that the samples according to the present invention retained both antistatic properties and electromagnetic wave shielding properties.

In displays in which accelerated electron rays are caused to strike on a fluorescent substance to display an image, e.g., cathode-ray tubes, the conductive antireflection film having

antistatic properties disposed on the front side of the image display area preferably has such conductive properties that the sheet resistivity thereof is about $1 \text{ k}\Omega/\square$ or lower. In order for the conductive antireflection film to have the ability to shut off electromagnetic wave emitted by the display so as to diminish adverse influences thereof on the human body, the film preferably has a sheet resistance of about $500 \Omega/\square$ or lower. It can be seen from these standpoints that the conductive antireflection films of the samples obtained in the Examples according to the present invention had such electrical performances sufficient for practical use.

As described above, the prior art problem that when an antireflection film having a multilayer structure comprising at least one metal film made of nickel alone or iron alone and one or more transparent dielectric films is subjected to heat treatment, the electrical resistance thereof is deteriorated (increased) can be eliminated by using a film of a nickel-iron alloy in place of the nickel or iron film. Namely, it was experimentally found that the alloy film surprisingly improves the stability of electrical resistance. Based on this unexpected effect, the present invention has been achieved.

The present invention brings about the following effects. Since the metal film as a constituent layer of the conductive antireflection films according to the present invention is a film of a nickel-iron alloy, the conductive antireflection films have excellent thermal stability. Because of this, the conductive antireflection films change little in transmittance or

reflectance through high-temperature heat treatment. Furthermore, since the metal film in each of the conductive antireflection films is a film of a nickel-iron alloy, the sheet resistivity thereof remains unchanged even after high-temperature heat treatment.

INDUSTRIAL UTILIZATION POSSIBILITY

The optical properties and electrical resistance of the conductive antireflection films according to the present invention are thermally stable. Even when a face glass plate coated with a conductive antireflection film according to the present invention is bonded to a funnel with a glass frit with heating, the performances possessed by the coated face plate before the bonding can hence be maintained. Therefore, a cathode-ray tube can be produced without impairing the optical properties or antistatic properties of the coated face plate.

SCOPE OF THE CLAIMS

1. A glass article having conductive antireflection coating, which comprises a glass substrate having a refractive index of from 1.4 to 1.7 as measured at a wavelength of 550 nm and a conductive antireflection film comprising superposed layers comprising, formed on the glass substrate in this order, a first layer which is a metal film, a second layer which is a high-refractive-index transparent dielectric film having a refractive index of from 2.0 to 2.4 as measured at a wavelength of 550 nm, and a third layer which is a low-refractive-index transparent dielectric film having a refractive index of from 1.35 to 1.46 as measured at a wavelength of 550 nm, said metal film being a film of a nickel-iron alloy, and said glass article having a visible ray reflectance of 1% or lower.

2. The glass article having conductive antireflection coating as claimed in claim 1, wherein the metal film has a nickel content of from 5 to 95% by weight.

3. The glass article having conductive antireflection coating as claimed in claim 1 or 2, wherein the metal film has a thickness of from 1.5 to 8 nm.

4. The glass article having conductive antireflection coating as claimed in any one of claims 1 to 3, wherein the high-refractive-index transparent dielectric film as the second layer has a thickness of from 5 to 140 nm and the low-refractive-index transparent dielectric film as the third layer has a thickness of from 50 to 120 nm.



5. A glass article having conductive antireflection coating, which comprises a glass substrate having a refractive index of from 1.4 to 1.7 as measured at a wavelength of 550 nm and a conductive antireflection film comprising superposed layers comprising, formed on the glass substrate in this order, a first layer which is a metal film, a second layer which is a high-refractive-index transparent dielectric film having a refractive index of from 2.0 to 2.4 as measured at a wavelength of 550 nm, a third layer which is a medium-refractive-index transparent dielectric film having a refractive index of from 1.7 to 1.9 as measured at a wavelength of 550 nm, and a fourth layer which is a low-refractive-index transparent dielectric film having a refractive index of from 1.35 to 1.46 as measured at a wavelength of 550 nm, said metal film being a film of a nickel-iron alloy, and said glass article having a visible ray reflectance of 1% or lower.

6. The glass article having conductive antireflection coating as claimed in claim 5, wherein the metal film has a nickel content of from 5 to 95% by weight.

7. The glass article having conductive antireflection coating as claimed in claim 5 or 6, wherein the metal film has a thickness of from 1.5 to 8 nm.

8. The glass article having conductive antireflection coating as claimed in any one of claims 5 to 7, wherein the high-refractive-index transparent dielectric film as the second layer has a thickness of from 5 to 70 nm, the medium-refractive-index transparent dielectric film as the third layer



has a thickness of from 10 to 100 nm, and the low-refractive-index transparent dielectric film as the fourth layer has a thickness of from 50 to 120 nm.

9. A glass article having conductive antireflection coating, which comprises a glass substrate having a refractive index of from 1.4 to 1.7 as measured at a wavelength of 550 nm and a conductive antireflection film comprising superposed layers comprising, formed on the glass substrate in this order, a first layer which is a metal film, a second layer which is a high-refractive-index transparent dielectric film having a refractive index of from 2.0 to 2.4 as measured at a wavelength of 550 nm, a third layer which is a metal film, a fourth layer which is a high-refractive-index transparent dielectric film having a refractive index of from 2.0 to 2.4 as measured at a wavelength of 550 nm, and a fifth layer which is a low-refractive-index transparent dielectric film having a refractive index of from 1.35 to 1.46 as measured at a wavelength of 550 nm, at least one of the metal films respectively as the first and third layers being a film of a nickel-iron alloy, and said glass article having a visible ray reflectance of 1% or lower.

10. The glass article having conductive antireflection coating as claimed in claim 9, wherein the nickel-iron alloy film has a nickel content of from 5 to 95% by weight.

11. The glass article having conductive antireflection coating as claimed in claim 9 or 10, wherein the metal films respectively as the first and third layers each has a thickness of from 1.5 to 7.5 nm and the total thickness of the metal films



is 9 nm or smaller.

12. The glass article having conductive antireflection coating as claimed in any one of claims 9 to 11, wherein the high-refractive-index transparent dielectric film as the second layer has a thickness of from 10 to 70 nm, the high-refractive-index transparent dielectric film as the fourth layer has a thickness of from 10 to 70 nm, and the low-refractive-index transparent dielectric film as the fifth layer has a thickness of from 70 to 120 nm.

13. The glass article having conductive antireflection coating as claimed in any one of claims 1 to 12, which has a transparent dielectric film formed between the glass substrate and the metal film as the first layer.

14. The glass article having conductive antireflection coating as claimed in any one of claims 1 to 13, wherein the glass base is a face plate made of glass for a cathode-ray tube.

15. A cathode-ray tube obtained by heat bonding the glass article having conductive antireflection coating of claim 14 to a funnel with a glass frit.

